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TEXAS The University of Texas at Austin

THERMODYNAMIC AND KINETIC SIMULATIONS AND TESTING PROCEDURES TO SCREEN FOR ENHANCED DURABILITY OF CONCRETE CONTAINING INDUSTRIAL WASTE

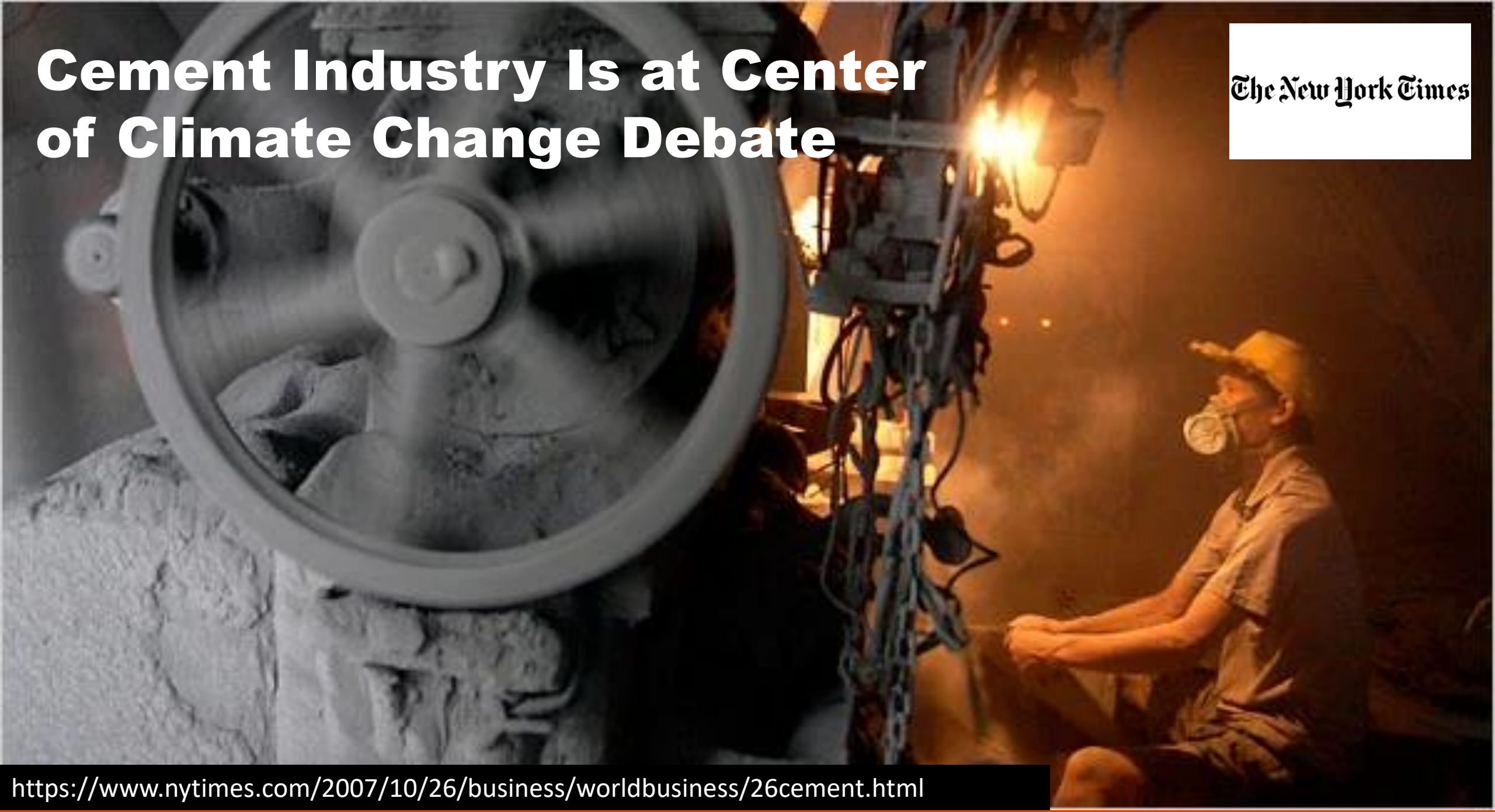
Maria Juenger, Lynn Katz, Farshad Rajabipour, Enrique Gomez,

Keshav Bharadwaj, Tongren Zhu, Yu Wang, Gopakumar Kaladharan, Yi-Chen Lan
Al Innis, Pablo Zavattieri, Burkan Isgor, Jason Weiss

October 14th 2021

https://www.nytimes.com/2007/10/26/business/worldbusiness/26cement.html

Cement Industry Is at Center of Climate Change Debate



The New York Times

https://www.nytimes.com/2007/10/26/business/worldbusiness/26cement.html

Change for the Future

- A change is needed in how concrete mixtures are designed
- We need a solution that addresses sustainability and performance that scales
- The time for change is now

- Three Prong approach

Photo 111003905 © Nopphinan Meephoka | Dreamstime.com

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IC Bridge Decks
~3% added cost
3x life, < cracking

Life Cycle Performance

Sustainability

Reduce Clinker

Reduce Cement Content

Photo 111003905 © Nopphinan Meephoka | Dreamstime.com

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Long-term work with groups to lower binder, as well as specifiers

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Life Cycle Performance

Sustainability

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Reduce Clinker

Reduce Cement Content

Todays talk is really looking at how we reduce clinker in the binder

Photo 111[illegible] pphinan Meephoka | Dreamstime.com

Research Framework

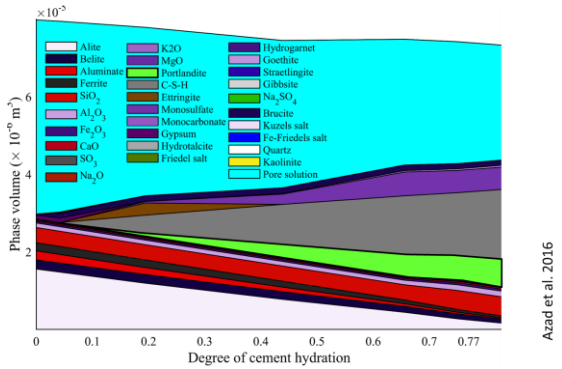
Screening Tools for IBM Evaluation: Provide Inputs for Thermodynamic/Kinetic Modeling

Kinetic Models for Dissolution and Reaction

Admixture Delivery to Alter Set or Deleterious Reactions

Thermodynamic Properties of Materials

Thermodynamic /Kinetic Model of Cementitious System Incorporating IBM



Scaling Models to Pore Structure

Scaling Models for Transport/ Durability

Scaling Models for Mechanical Properties

Service Life Prediction

Weiss et al. 2018

Thermodynamic Modeling of OPC and SCM Systems

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+

We need to know the volumes of the materials that would be mixed together (Mixture proportions)

Photo 19158807 © Zoran Mijatov

Thermodynamic Modeling

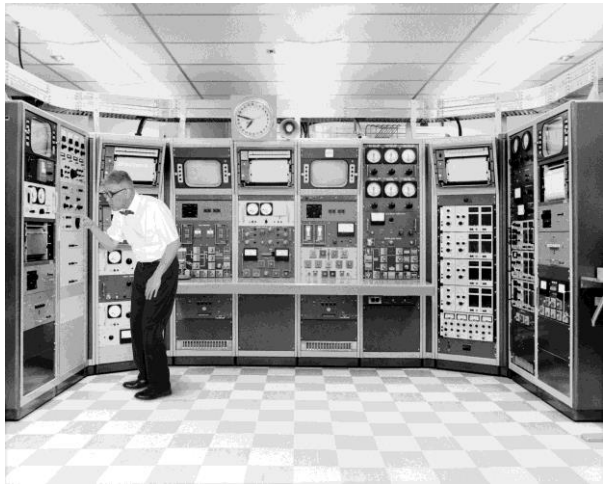

Photo 116022050 © Wisconsinart

Photo 44066082 © Luchschen | Dreamstime.com
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Modeling framework

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PASTE

OPC amount and chemical composition

(C3S, C2S, C3A, C4AF, Na2O, K2O, etc.)

+

SCM amount, chemical composition, maximum reactivity

(SiO2, Al2O3, CaO, Na2O, K2O, SO3, etc.)

INPUT

Amounts of OPC and SCM oxide phases @ a given time or degree of hydration

+

Amount of water

GEMS

Pozzolanic reactivity test (maximum degree of reactivity)

Kinetic model for OPC and SCM

Pozzolanic Reactivity Test (PRT)

Modified Parrot and Killoh Model (MPK)

CONCRETE

Modified Pore Partitioning Model

PASTE OUTPUT

Solid phases: C-S-H, CH, Aft, Afm, etc.

Pores: Chemical shrinkage, gel pores, capillary pores)

Pore solution: Composition, pH, resistivity

+

Aggregate

Concrete resistivity

Formation factor

Porosity

Strength

Modeling framework

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Aggregate

Concrete resistivity

Formation factor

Porosity

Strength

Compatible with
FHWA PEM/PRS Specs
AASHTO PP-84

Pozzolanic Reactivity Test

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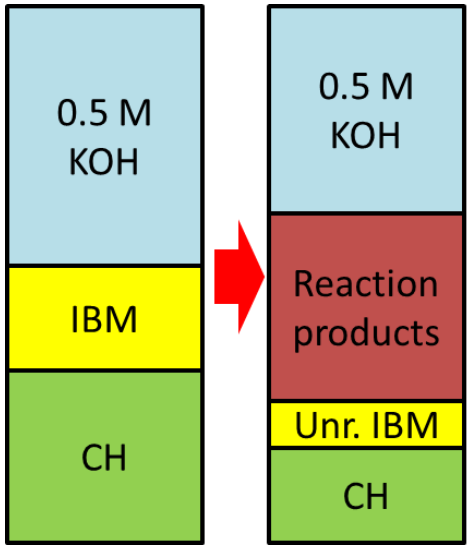
Pozzolanic reactivity test ("PRT") can determine reactivity of the IBM

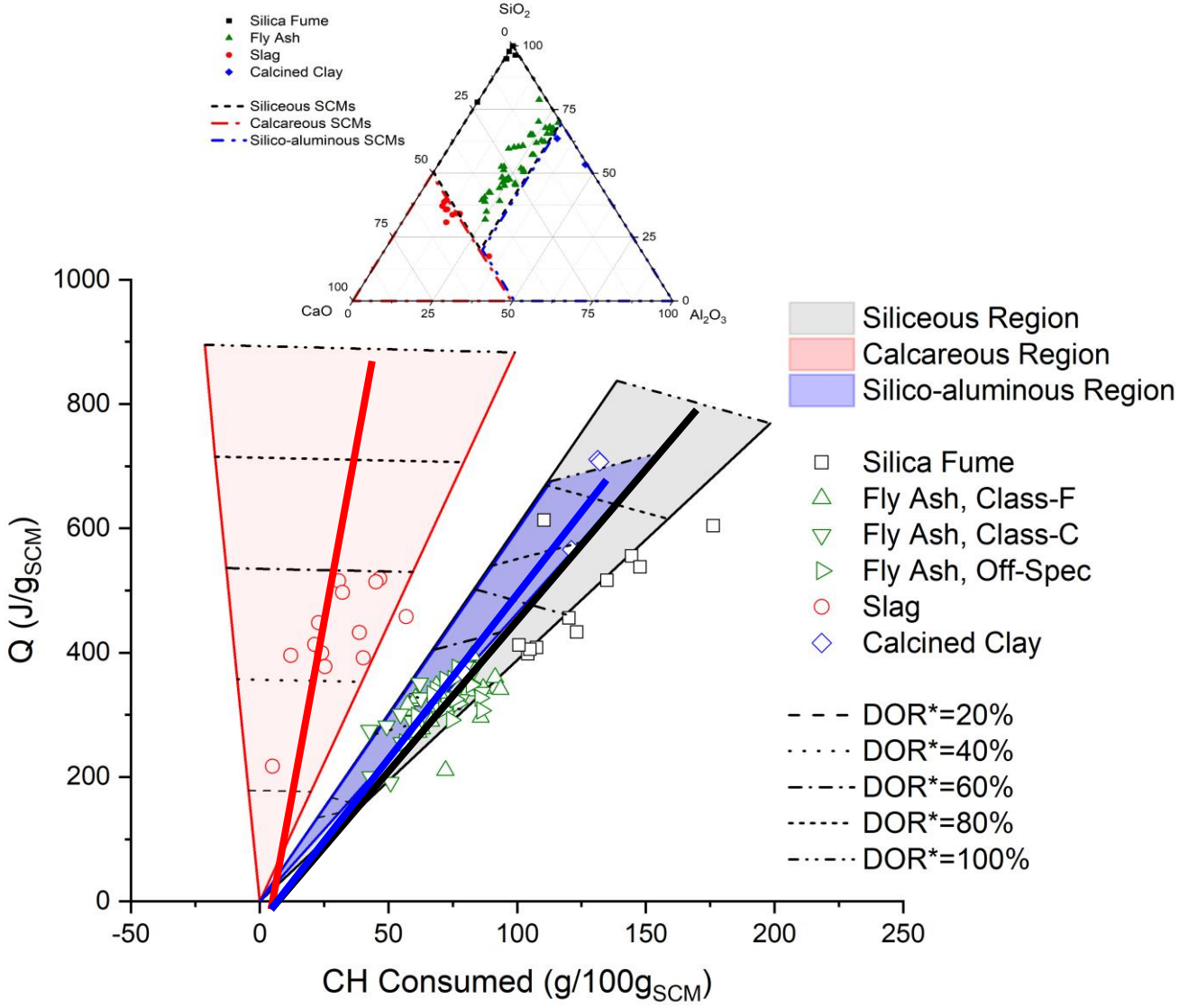
Input into the model



$$\text{IBM} + \text{CH} + \text{H}_2\text{O} \rightarrow \text{reaction products} + \Delta$$

↑ Measure CH Consumed

↑ Measure Heat Released



Demonstration of Approach
Caltrans Specification Change

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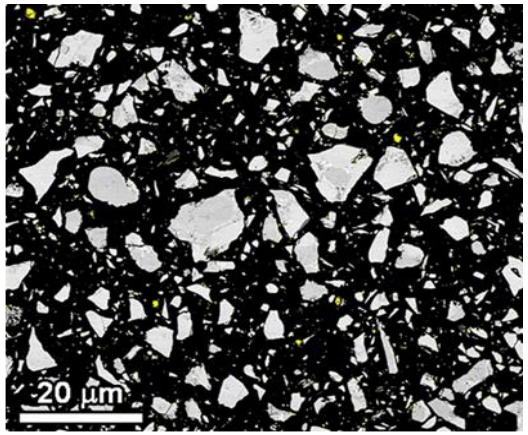
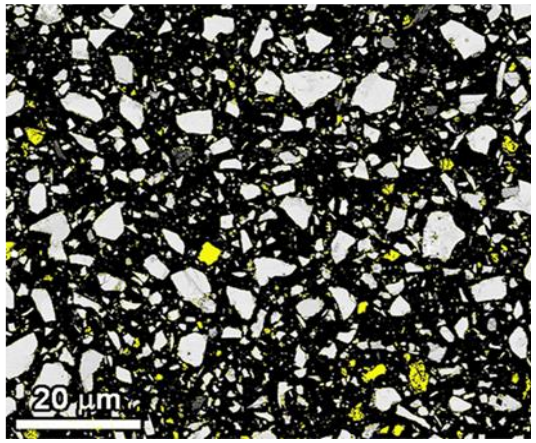
OPC - ASTM C150

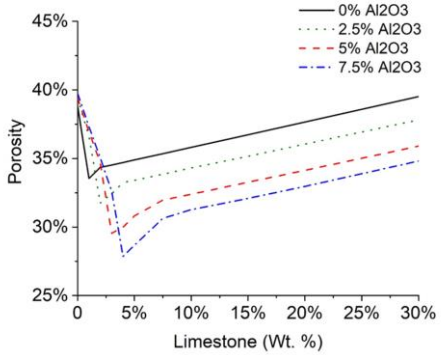




PLC - ASTM C595 IL

- Generally, there is about 10% more limestone in C595 than C150
- C595 cements are an ‘engineered system’
  - Not simply diluting the cement
- C595 cements are finer
  - Accelerated rate of reaction (overcomes dilution)
  - Limestone is softer than clinker – therefore finer
- C595 cements can have some advantages – space filling, nucleation, chemical reactions

PLC+ SCM



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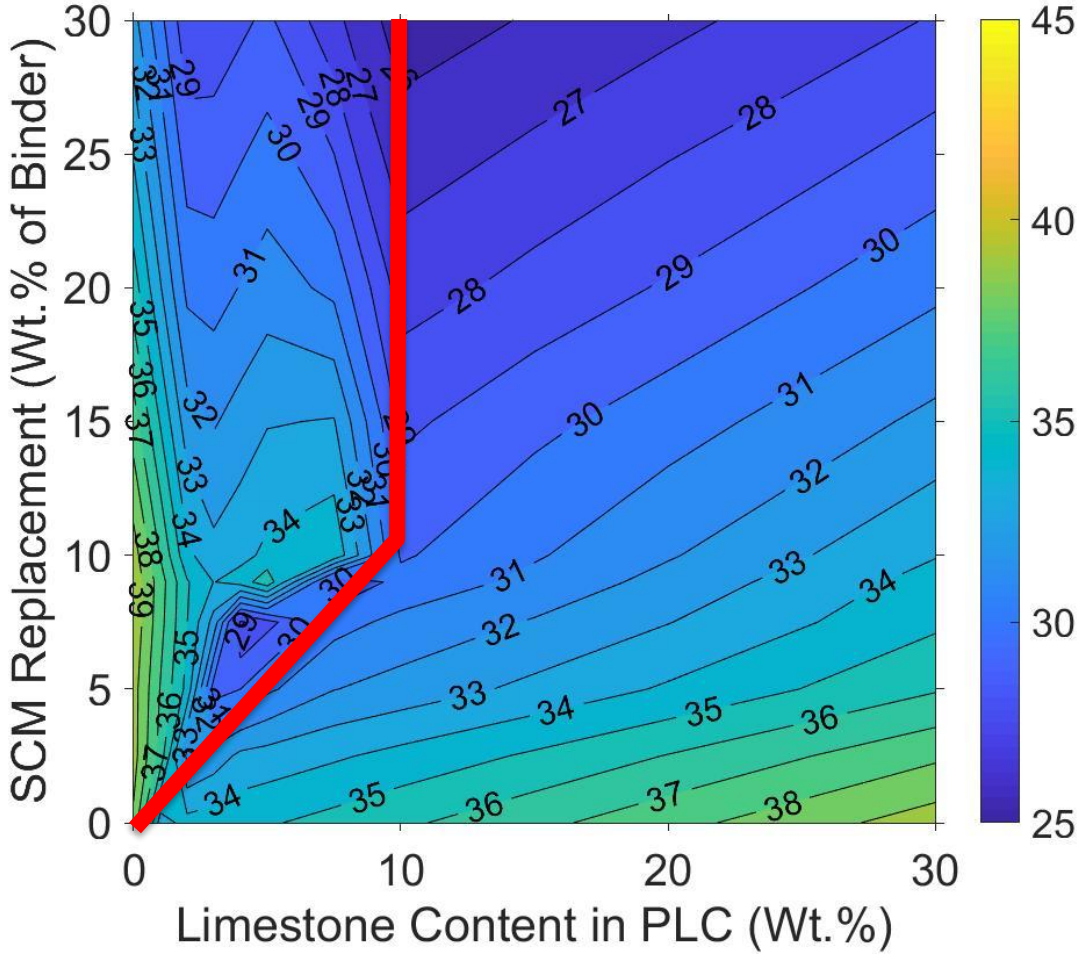
Can SCM be used with PLC?

- Porosity w/ 100% Al_2O_3 addition
- ~ 38 to 39% porosity occurs
- Low porosities can be obtained when PLC+SCM is used
- Translates into performance
- Specification change
- Mixture design/prediction (PP-84)
- Call with numerous SHA, interest



Bharadwaj et al. 2021

Photo 72394692 / Faq © Weerapat Wattanapichayakul | Dreamstime.com

Modeling framework

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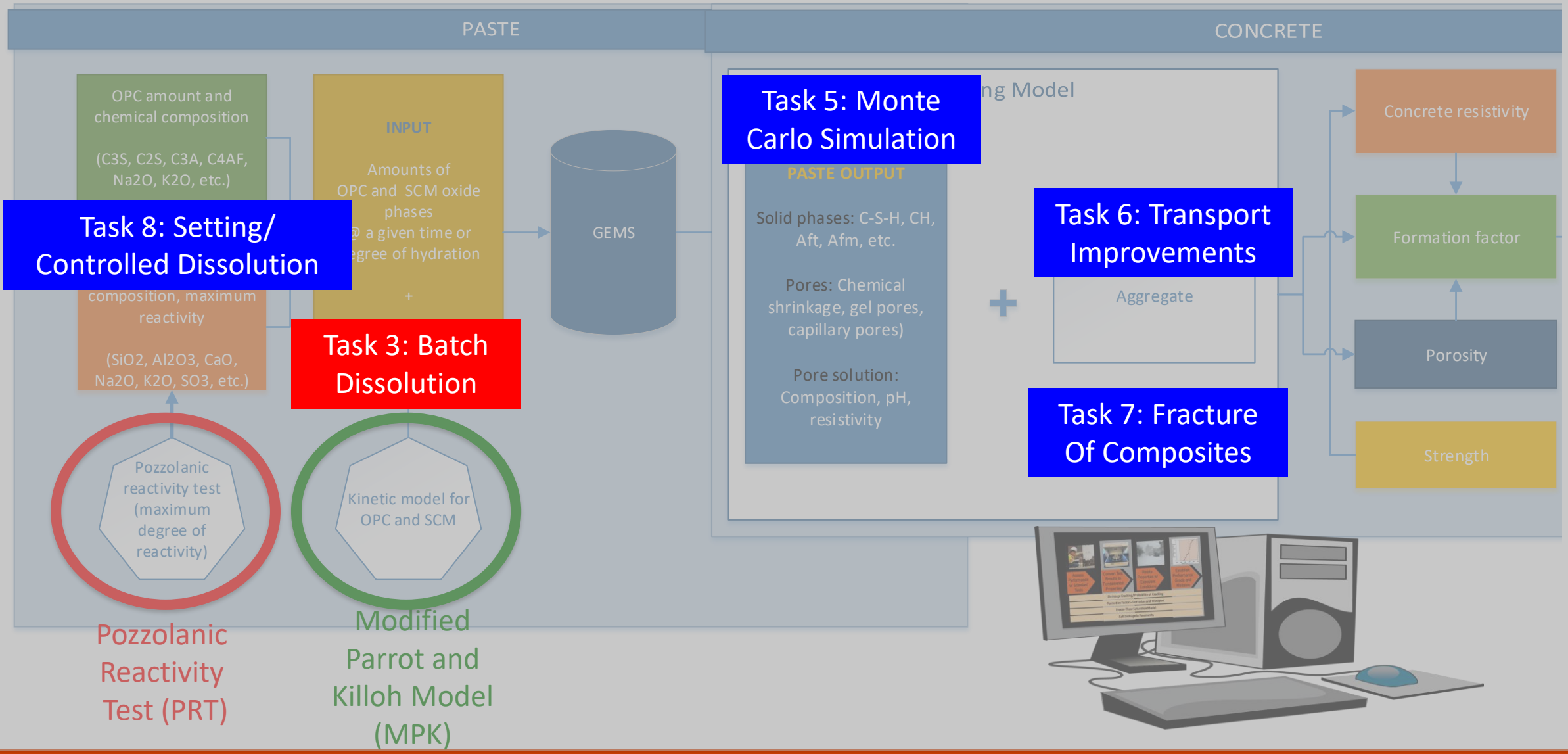


Task 8: Setting/ Controlled Dissolution

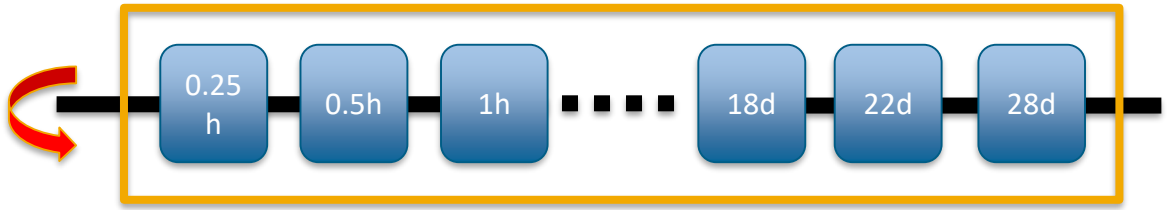
Task 3: Batch Dissolution

Task 5: Monte Carlo Simulation

Task 6: Transport Improvements

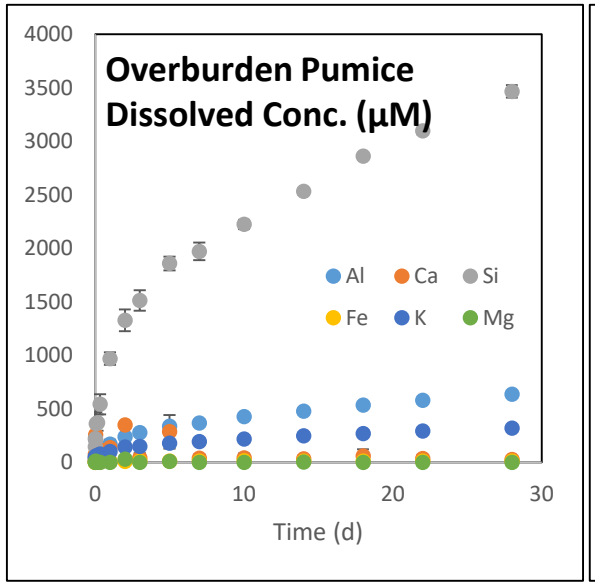
Task 7: Fracture Of Composites

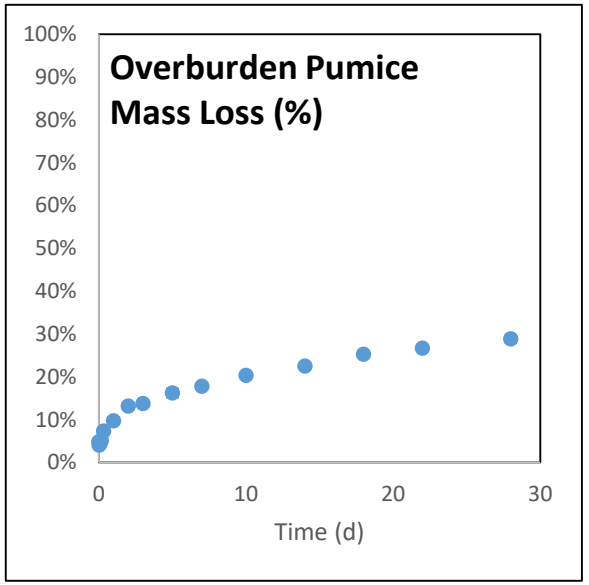
Batch Dissolution of IBM in Simulated Pore Solution Gives Composition of Dissolved Phases

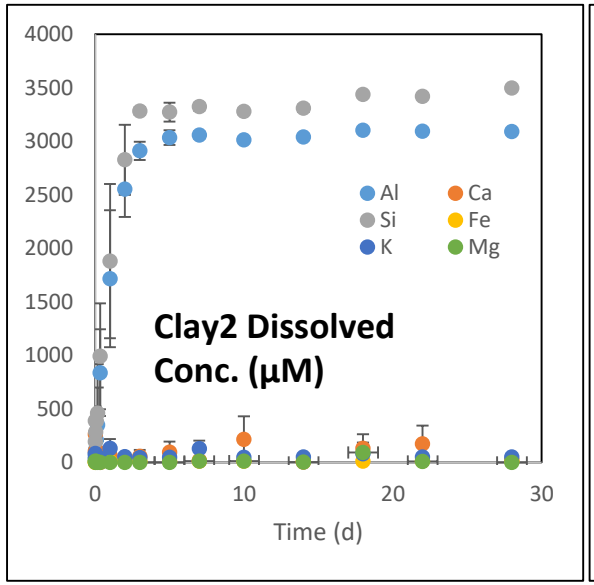


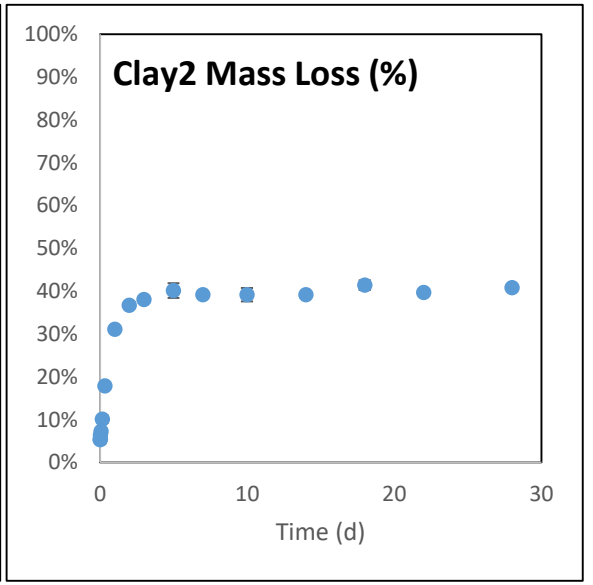
- IBMs added into solution in N_2 filled glove bag
- Rotate in tumbler; open one bottle at a time

Example Dissolution Behavior of Selected IBMs



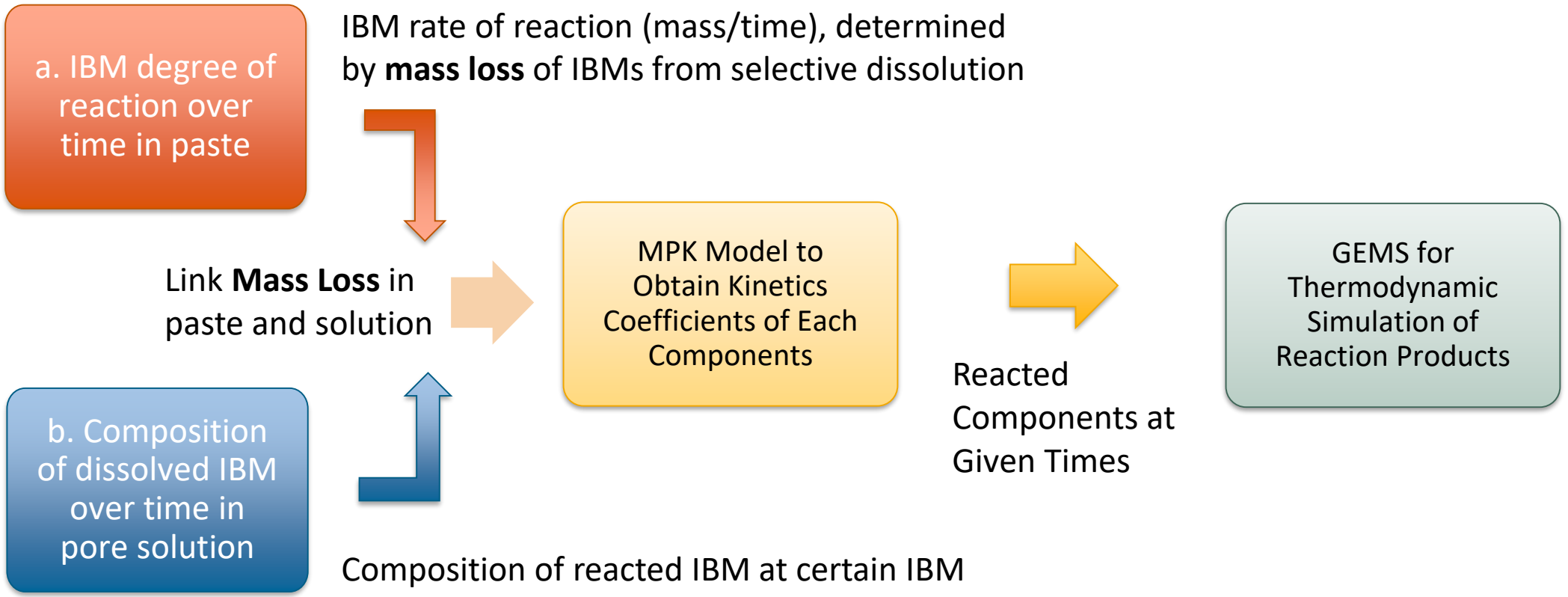






- Overburden Pumice kept dissolving, all data can be used to quantify reactivity of amorphous
- Clay 2 contains calcined kaolinite with quartz
- Its dissolution plateaued after about 7 days

Next Step: Link Mass Loss of IBM in Paste to Mass Loss of IBM in Simulated Pore Solution Dissolution



Modeling framework

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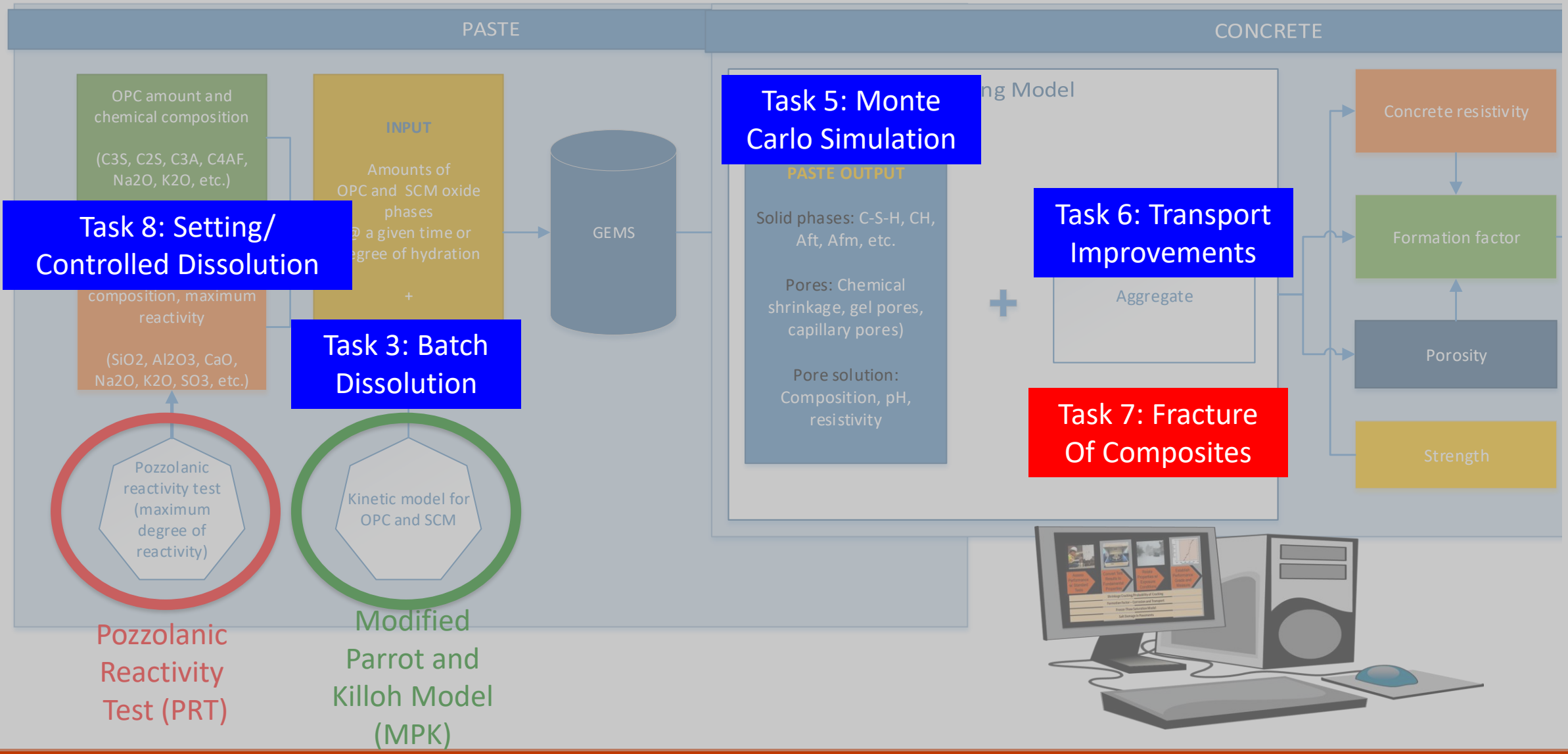
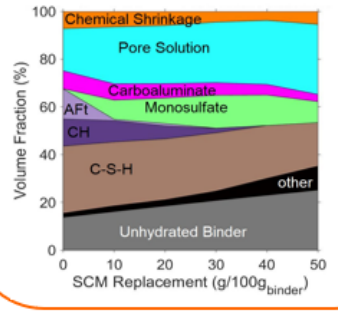


Multiscale Computational Models for Mechanical Properties

Thermodynamic Model

Inputs
- OPC & SCM compositions
- SCM reactivity
- Mixture proportions

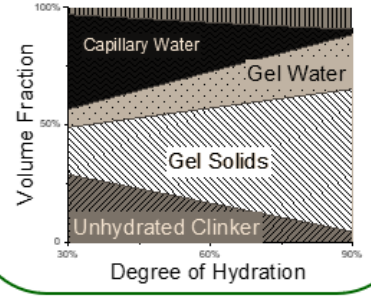
Outputs
- Volume of reaction products
- Pore solution composition



Pore Partitioning Model (PPM)

Inputs
- Thermodynamic model outputs

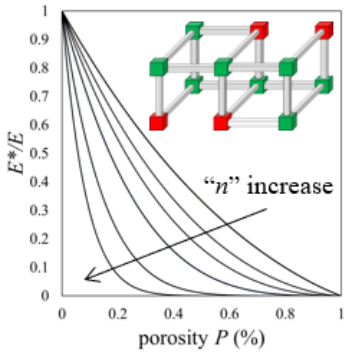
Outputs
- Volume fractions of reaction products
  - Gel water, capillary water
  - Gel solid
  - clinker
- Pore solution composition



Property-Porosity Relations

Inputs
- PPM outputs

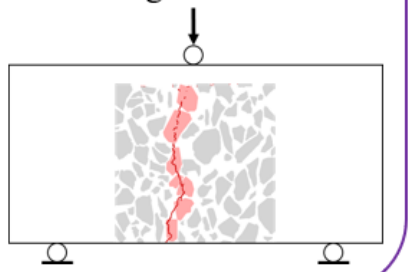
Outputs
- Elastic modulus development of paste
- Tensile strength development of paste
- Fracture toughness development of paste



FEM-based Mechanical model

Inputs
- Property-porosity relations outputs
- Mechanical properties of aggregate

Outputs
- Tensile strength of paste under B3B loading
- Flexural strength of mortar under 3PB loading



Multiscale Computational Models for Mechanical Properties

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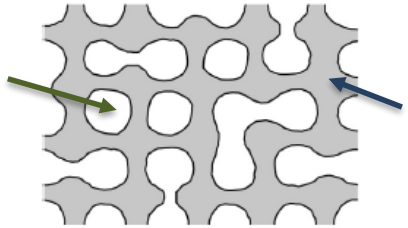
Mechanical properties of paste
E, σ_f, G_{Ic}

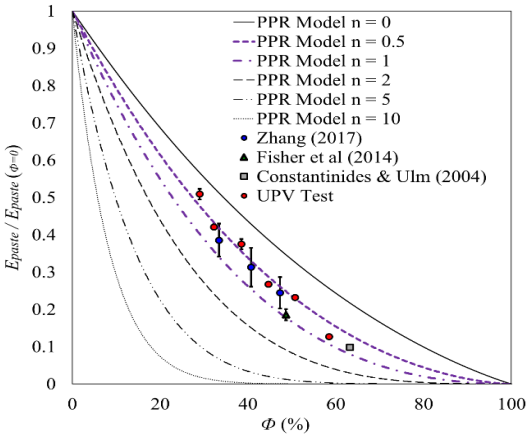
Property-Porosity Relationship

Pore
no mechanical properties

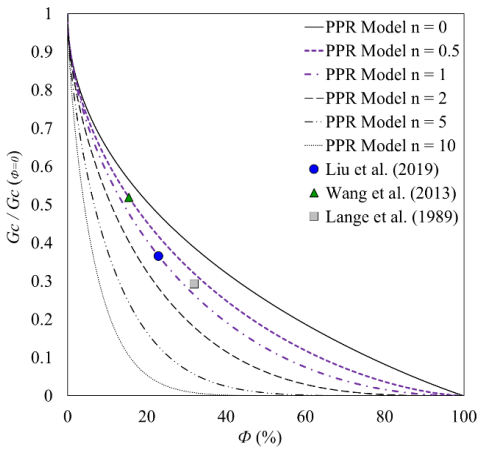


Solid
mechanical properties
E, σ_f, G_{Ic}

Elastic Modulus



Fracture Energy

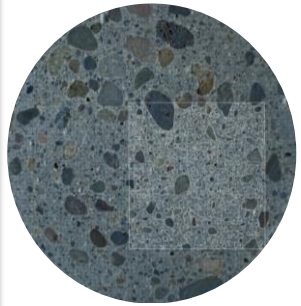


E0, Elastic modulus at 0 porosity
G0, Fracture toughness at 0 porosity

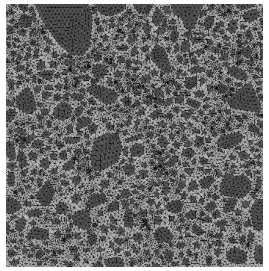
n, Disconnections parameters
ϕ ,Paste Porosity

FEM-based Mechanical model

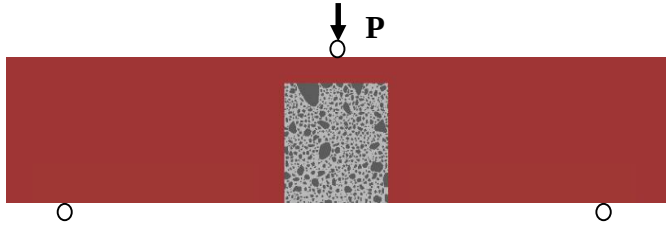
AutoCAD sketch

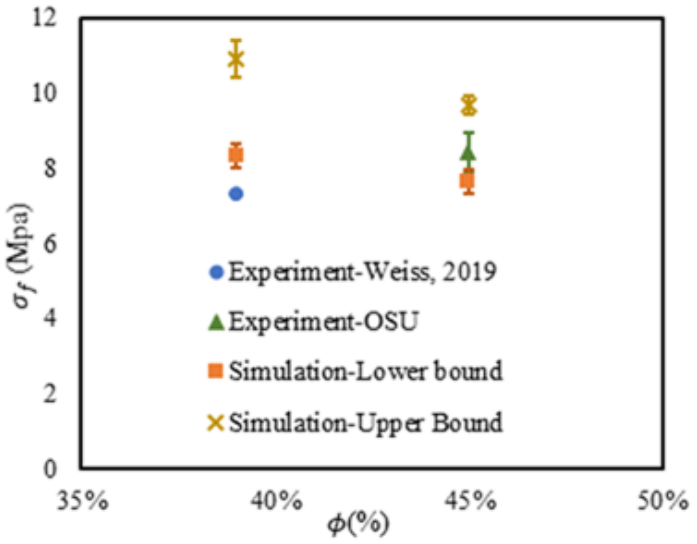


Abaqus mesh

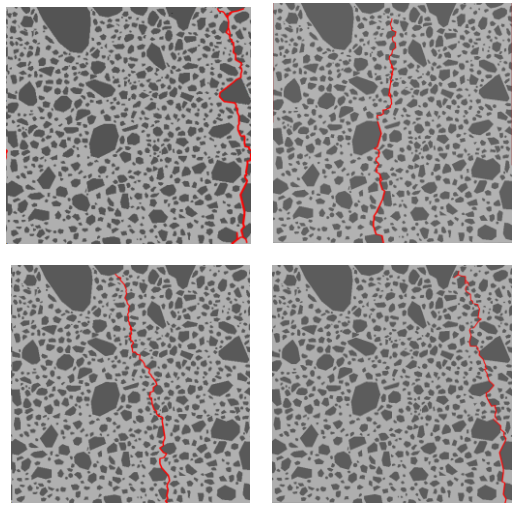


Three-point bending FEM model





Crack pattern evolution



Modeling framework

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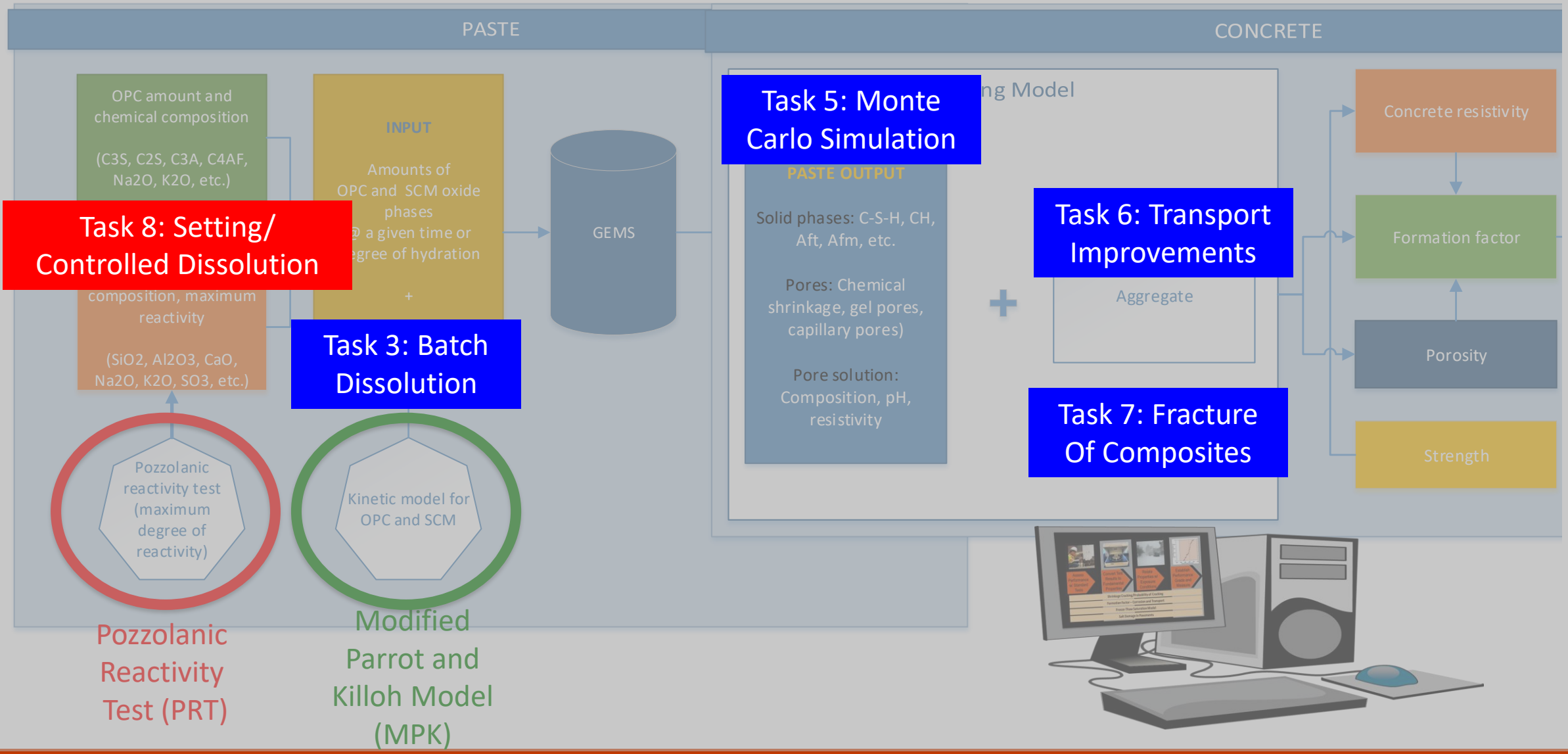
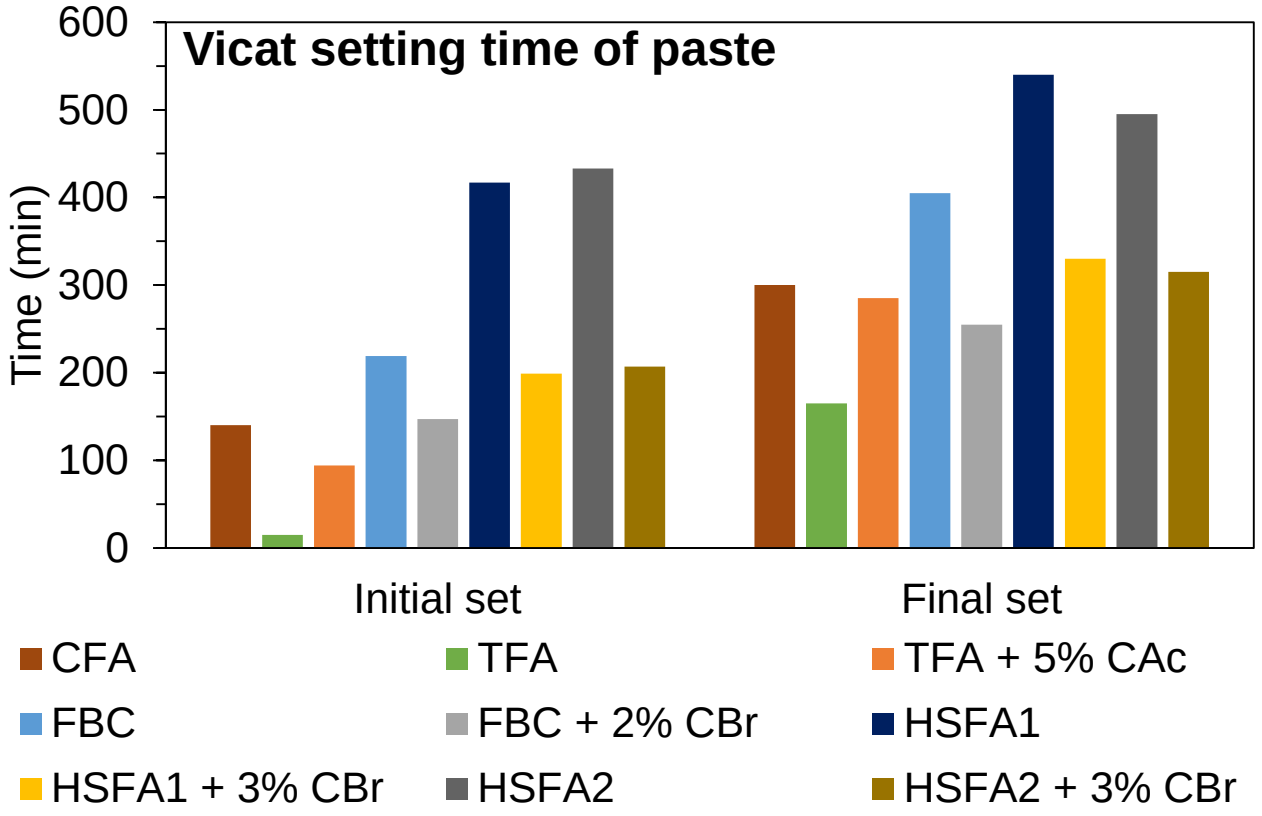
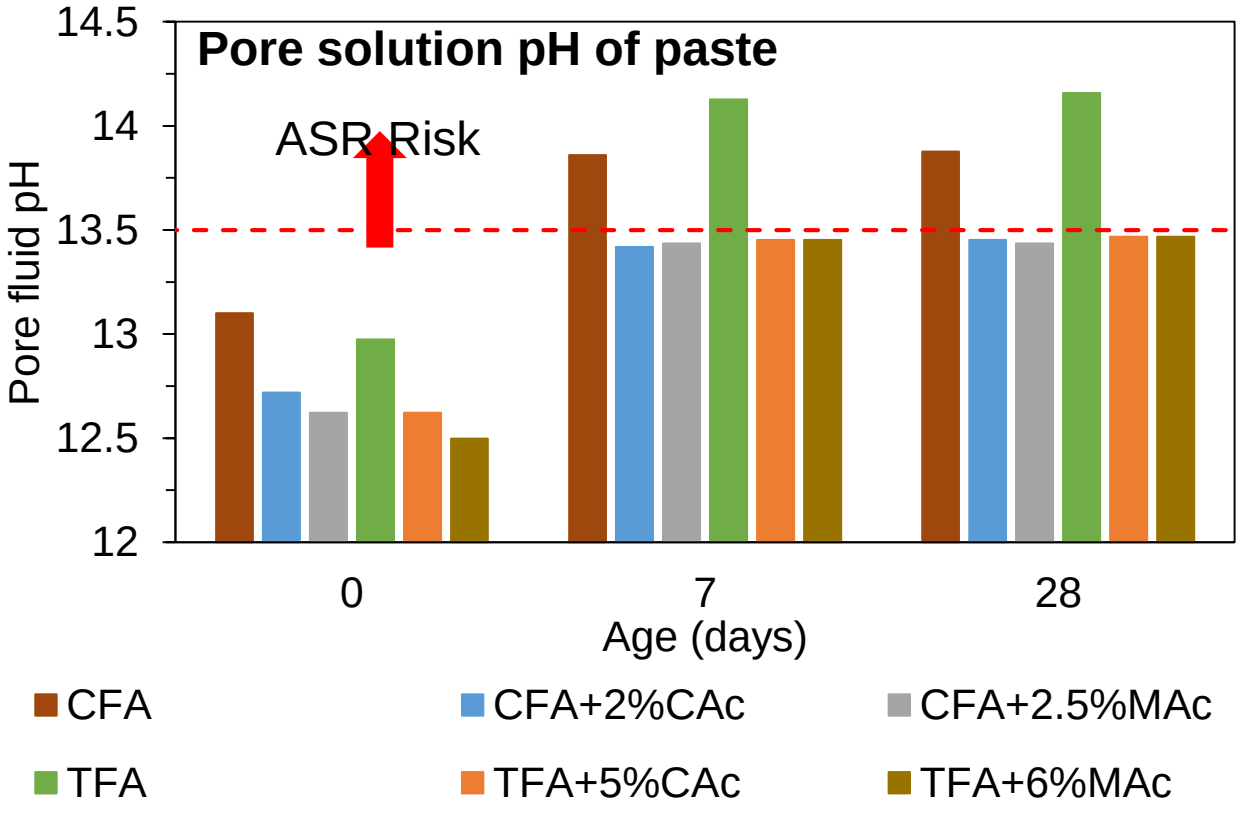


Off-spec high sulfur fly ash can affect concrete performance significantly; suitable beneficiating admixtures were developed





CFA Control fly ash

TFA Trona-impacted fly ash (high sulfur and alkali)

HSFA1/2 High sulfur fly ash with hannebachite

FBC Fluidized bed combustion ash (high sulfur – anhydrite)

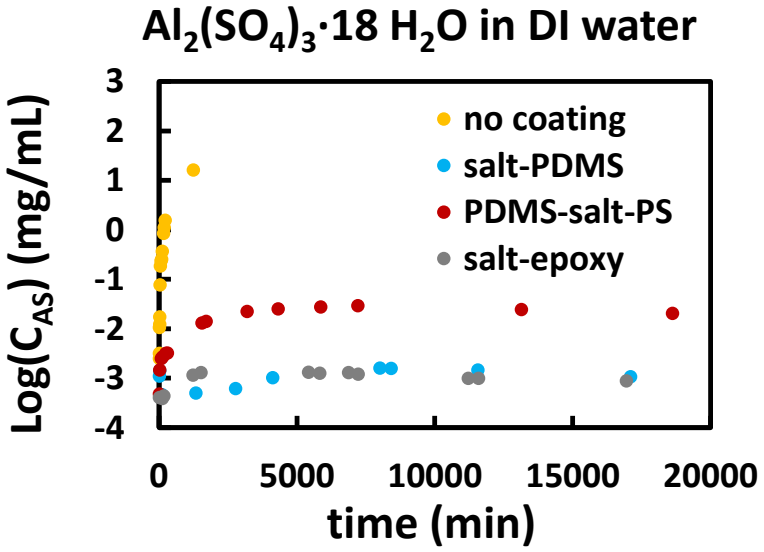
CAc Calcium acetate (reduces pore solution pH and prevents flash set due to Na_2CO_3)

MAc Magnesium acetate (reduces pore solution pH)

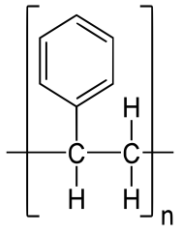
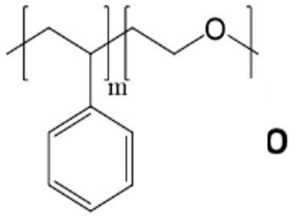
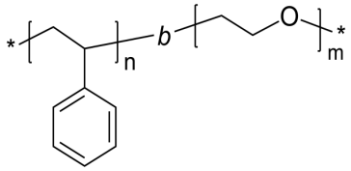
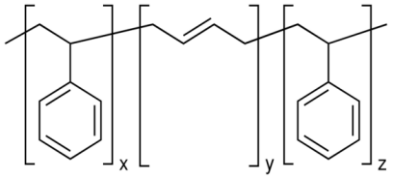
CBr Calcium bromide (accelerator)

Development of polymer barriers and coating methods for controlling dissolution kinetics and triggered release

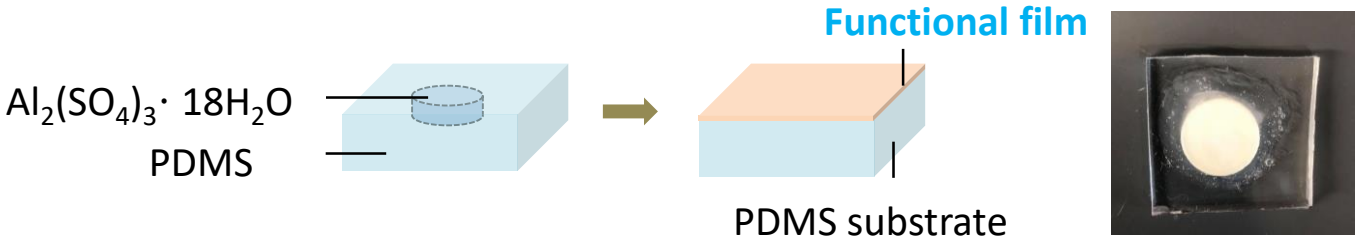
Potential polymer coatings capable of delaying admixture delivery **over 100-fold in terms of time**.



Potential polymers capable of **ion transport** or are **degradable** at high pH for delayed dissolution.

Barrier polymer	Complexing polymer	Degradable polymer	Rubbery polymer
			
Poly(styrene) (PS)	Polystyrene-block-polyethylene oxide (PS-PEO)	polystyrene-block-polylactic acid (PS-PLA)	Polystyrene-block-polybutadiene (PS-PBD)

@pH=4	control	Salt-PDMS	PDMS-salt-PS	Salt-epoxy
Time (min)	159	17092	18615	16943
		> 100-fold	> 100-fold	> 100-fold



Modeling framework

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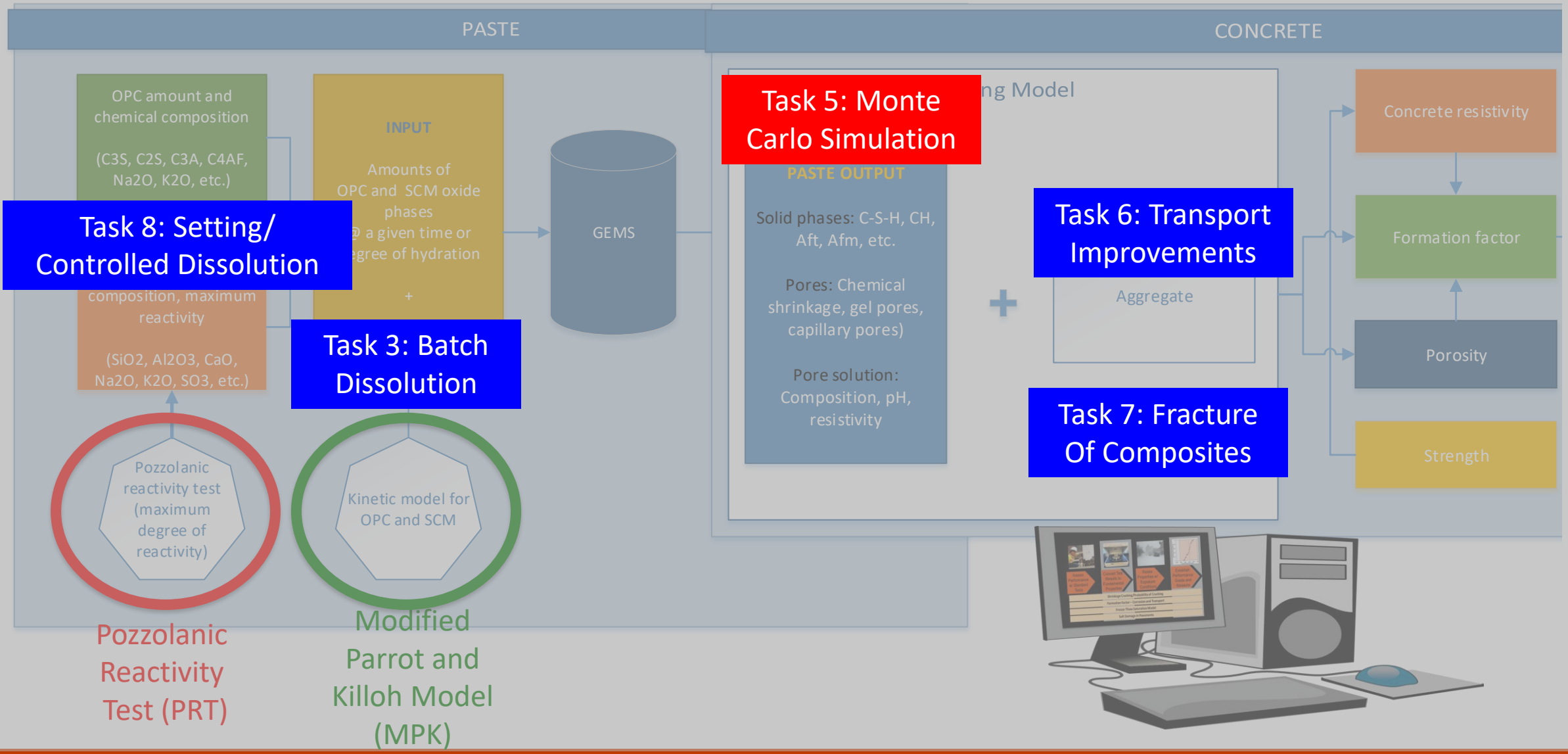
College of Engineering



Monte Carlo Simulations & Couple C-(A)-S-H Models

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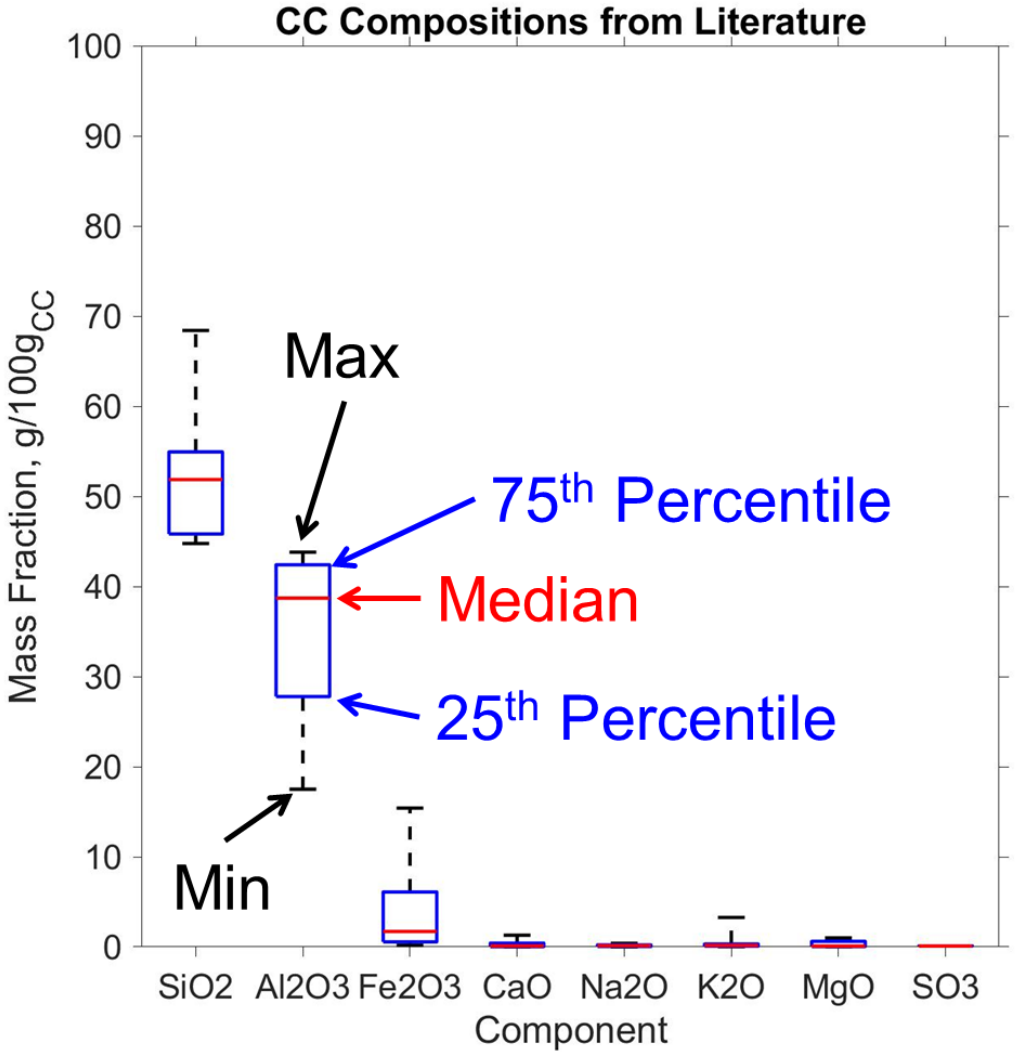
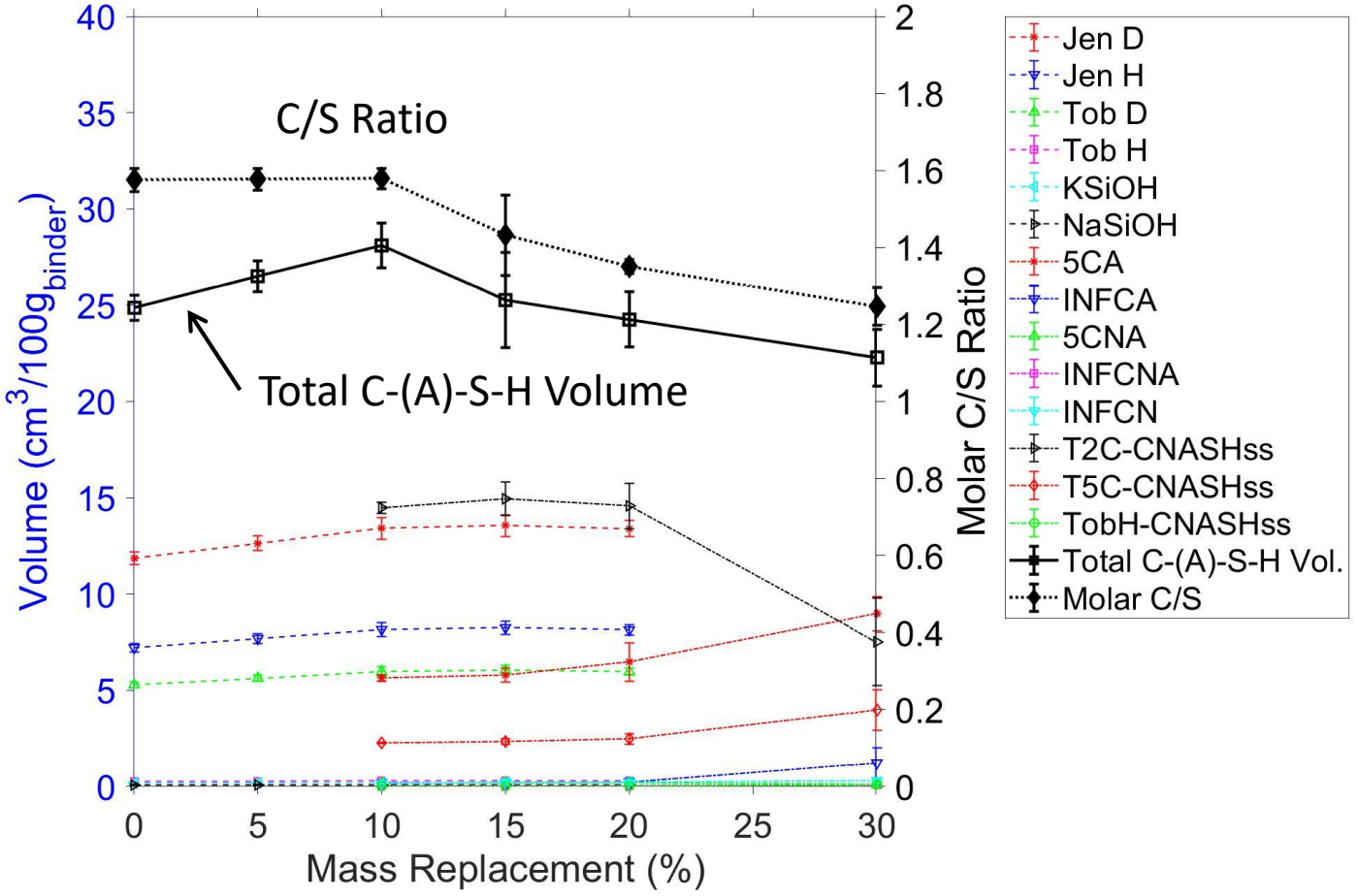
College of Engineering

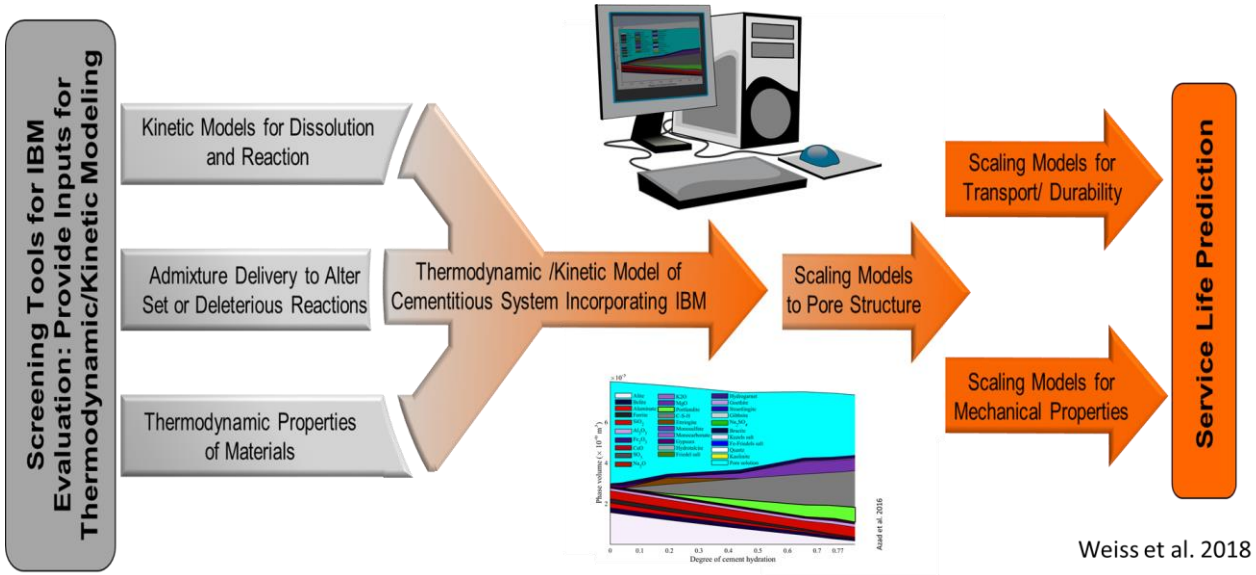




It is important to use the right CSH model !

Summary

- This project focused on developing the pozzolanic reactivity test (PRT) to evaluate industrial by products for use in concrete
- Update of kinetic modeling that is essential for SCM
- Illustrate value for Caltrans specifications (PLC + SCM)
- Updating dissolution models
- Porosity to strength models
- As setting and admixtures to relate dissolution
- Monte carlo simulations

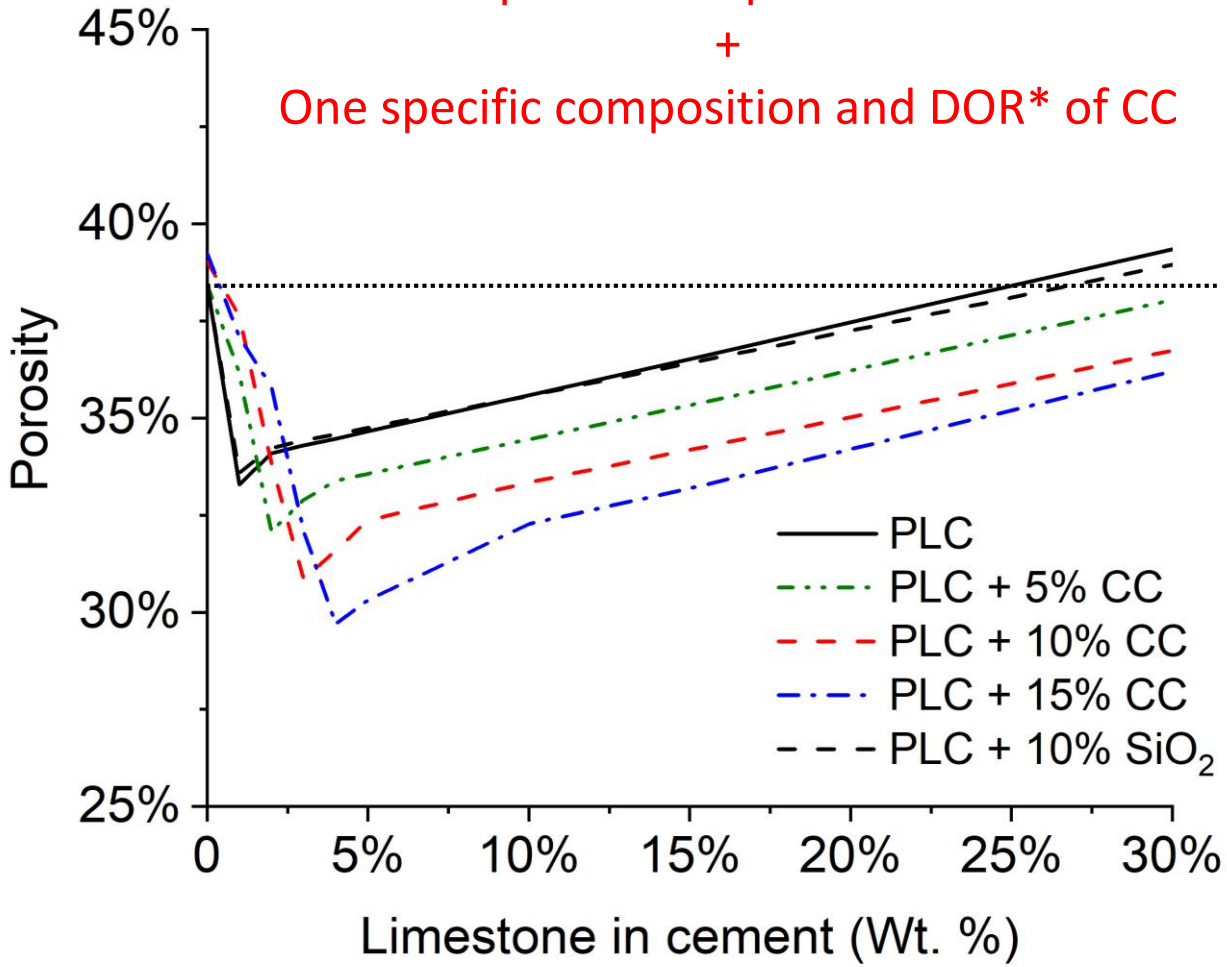
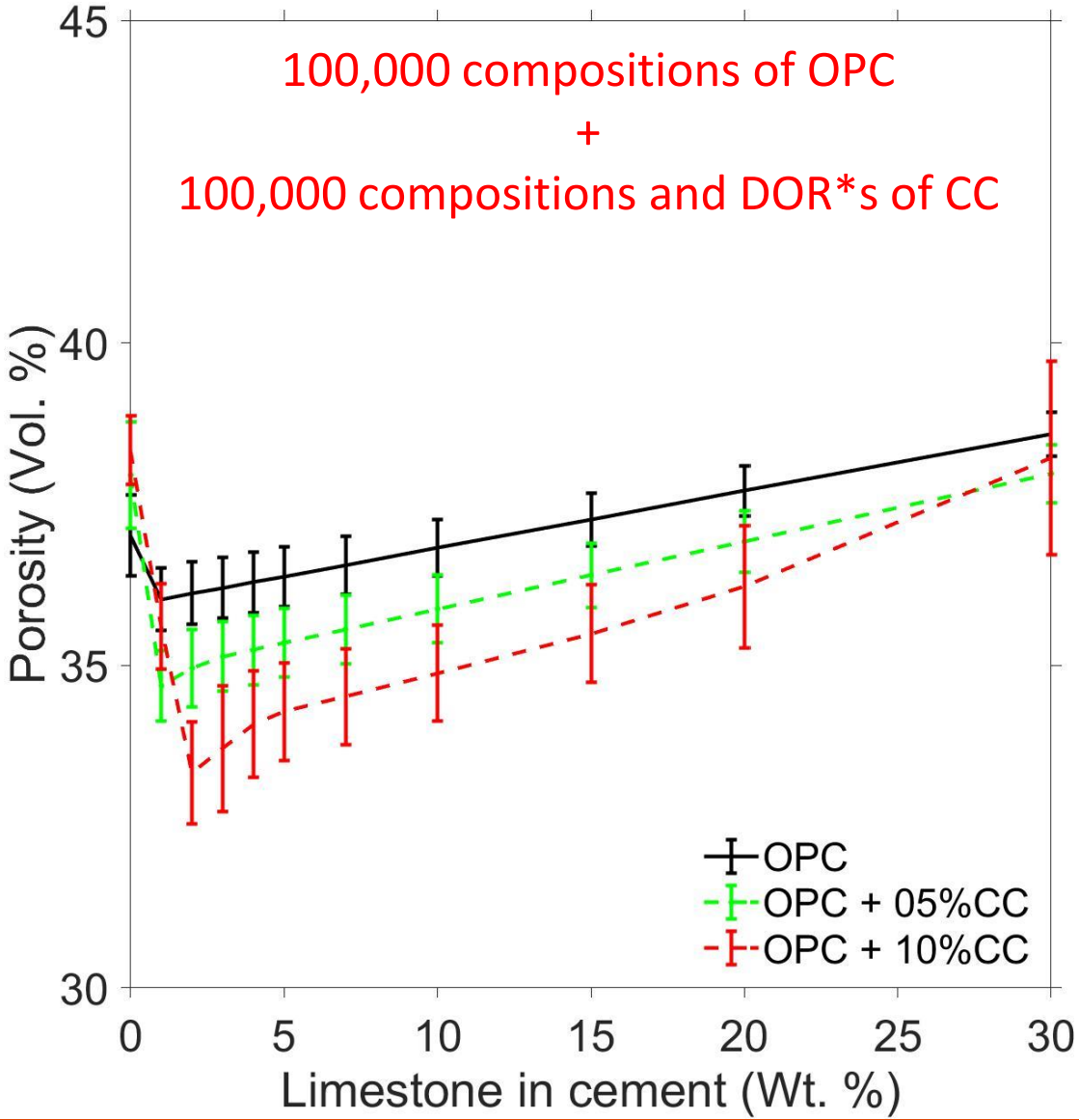


Weiss et al. 2018

Example Results: Porosity

Oregon State University

One specific composition of OPC
+
One specific composition and DOR* of CC



100,000 compositions of OPC
+
100,000 compositions and DOR*s of CC